



# Hg, $O_3$ , $\square_{abs}$ , $\square_{ext}$

Major Science Questions  
of the Next Decade  
that require SOFIA Sampling



# Where SOFIA Sampling Strategies are Required



- Questions address basic national/international needs and follow from NASA's (evolving) mission
- Repeated sampling opportunities: "traceable-standard" technology *and* technological advancement
- Vertical profiles and long UT/LS "random" sampling paths reachable from Ames
- Support or critically augment "Global View" (as aided by the "View from Space")



# Scientific Questions related to radiative forcing $O_3$ , $\Delta_{abs}$ , $\Delta_{ext}$

- Basic absorption and scattering properties of the Northern Hemisphere aerosol
- Relative Humidity environment for aerosol nucleation and ice occurrence
- Provide continuity and vertical structure for space-borne  $CO_2$ ,  $H_2O$ , other gases
- Measure tracers of vertical/meridional exchange:  $Rn$ ,  $Kr$ ,  $SF_6$ ,  $CH_3I$  or ...  $CH_3ONO_2$



# Scientific Questions related to radiative forcing $O_3$ , $\Delta_{abs}$ , $\Delta_{ext}$

Tropospheric Ozone and OH radical as they respond to pollution and climatic forcing will remain

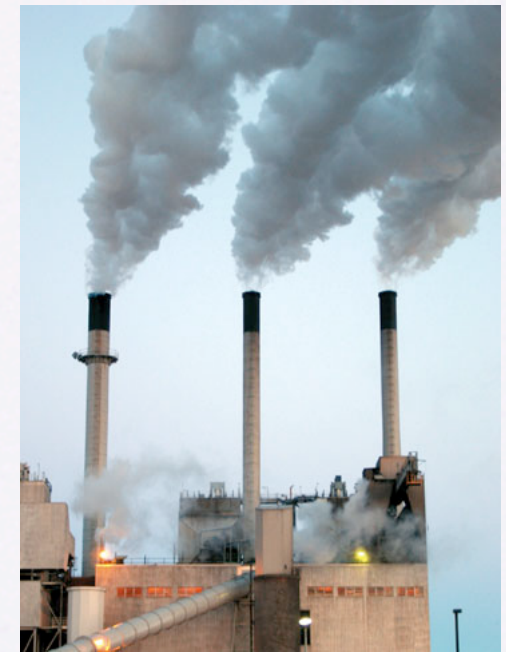
- Study  $O_3$  but also key  $O_3$  processes
- $O_3$  production and loss can be quantified by measuring  $NO_x$ ,  $HCHO$ , and  $HOOH$
- CO also provides *some* source information



# Mercury, an unexpected example



# Hg



(Photograph by Phillip J. Redman, U.S. Geological Survey).

- The national/international need to understand Hg is based on the toxicity of methyl mercury,
- ... its known sources from coal-fired power plants in North American (major economic concern)
- and its extremely puzzling locus of attack: Artic Sea and South Florida ??
- It also seems to have a connection with global transport and the stratosphere



# Hg



Mercury is a useful element found in such household items as thermometers and batteries. When converted to an organic form such as methylmercury, however, it can become hazardous.

## Mercury Poisoning from Fish Examined

**Contamination Seen As Global  
Problem Lasting for Centuries**

*By Catherine Carlock Simpson*

### **Fish consumption advisory still posted for upper Ouachita River**

In August 1992, the Louisiana Department of Health and Hospitals (DHH) and DEQ issued a health advisory regarding consumption of fish from the Ouachita River. That advisory remains in effect.

**"WILL MY GRANDCHILDREN GET** sick if they swim in the Ouachita River?" - "How does mercury get into fish?" - "Is it safe to eat catfish from bayous in south Louisiana?" - "How can I tell if I have mercury poisoning?"

These and other questions are being asked by people across the state following recent news media coverage about mercury contamination in fish from north Louisiana waters. In reality, however, the problem is not new and is not limited to Louisiana or even North America.

- shamelessly ripped from <http://www.leeric.lsu.edu/le/health/mercury.htm>



# Hg

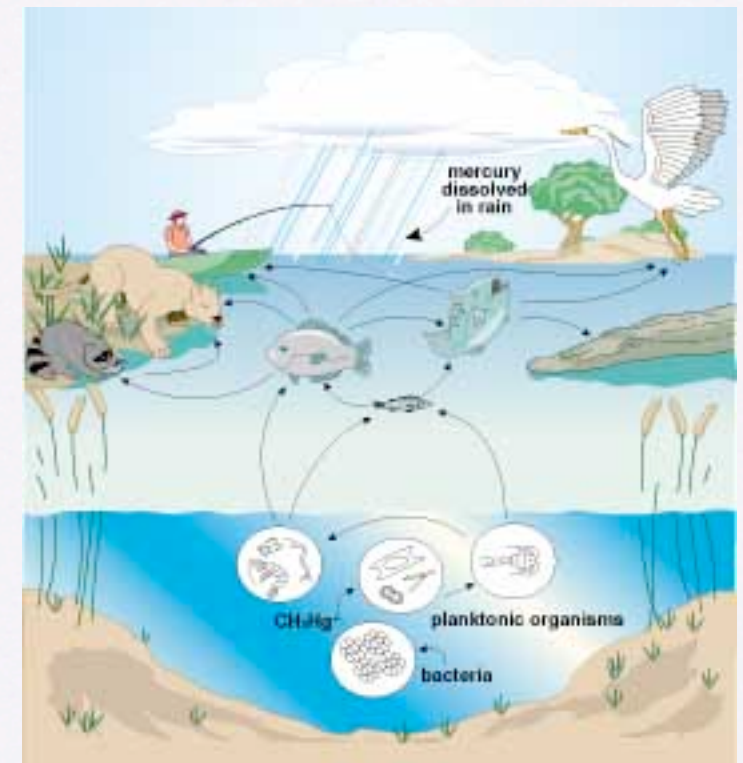


- *The effects of poisoning can be excruciating*
- *Methyl mercury attacks the cerebellum, which coordinates the movements, and destroys the personality*



# Hg

- Mercury's pathway into Everglades wildlife primarily begins in the skies, with mercury-loaded rainfall. Sulfate-reducing bacteria, mainly living in sediments and in mats of floating algae, absorb rainwater mercury and turn it into its organic form, methylmercury



(CH<sub>3</sub>Hg<sup>+</sup>). Microorganisms which eat such bacteria feed successive populations of larger organisms in the food web. At each step, methylmercury levels get concentrated. For wetland-dependent animals such as wading birds, raccoons and some panthers, concentrations can reach dangerously high levels. (BRUCE HALL ILLUSTRATION) □

- <http://www.research.fsu.edu/ResearchR/fallwinter97/features/midst.html>



# Classes of Hg: Alexey Ryaboshapko

*LTR Workshop, Ann Arbor, 2003*

## Mercury characteristics in the atmosphere

Mercury form	Life-time	Removal characteristics
Gaseous Elemental Mercury - GEM $\text{Hg}^0$	Year	Weak uptake by plants; No direct washout; Slow oxidation
Total Particulate Mercury - TPM	Few days	Uptake as a function of size, wind, surface conditions; Effective washout; No chemistry
Reactive Gaseous Mercury - RGM	Few days - hours	Effective uptake; Effective washout; Fast chemical reactions
Mercury Organic Compounds - MOC	Hours - minutes	No uptake; No washout; Fast destruction



# Hg Sources



- *Incineration facilities ... considerable local sources*
- *Coal mining in the US ... EPA Concern, ... stringent rules*
- *Coal mining in developing countries with expanding energy requirements: China, E. Europe (shown)*
- *Likelihood of growth over the next decades!*
- *<http://www.news.harvard.edu/gazette/2003/01.30/01-mercury.html>*



# Distant Hg Sources



- *Gold mining in the Amazon, also other S. American and African countires*
- *A source not considered relevant to Northern problems*

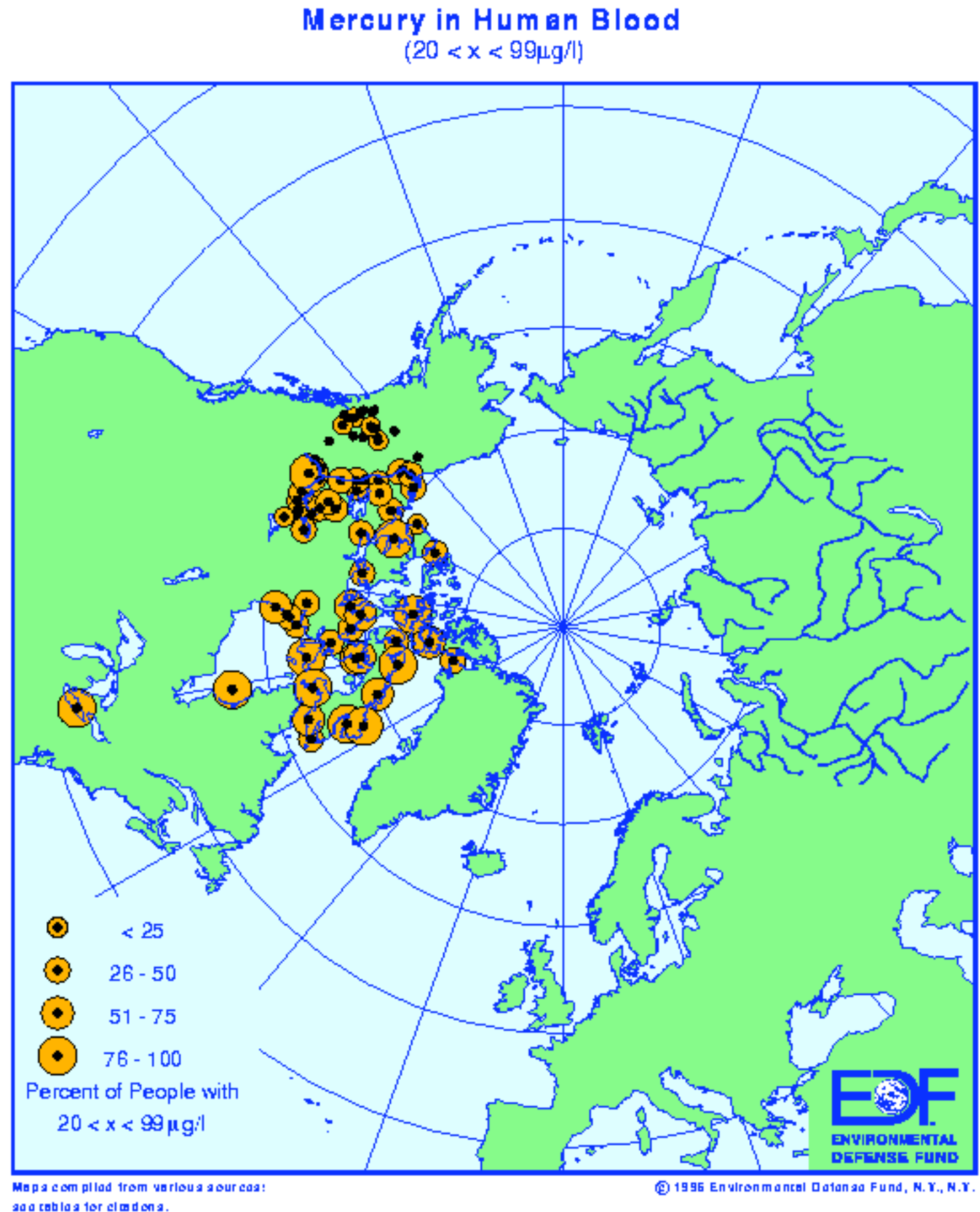
- *<http://www.news.harvard.edu/gazette/2003/01.30/01-mercury.html>*
- *<http://www.iisec.ucb.edu.bo/landersen/amazon.htm>*



# Hg in the Arctic

[rainbow.lidgo.columbia.edu/  
text/mercury.html](http://rainbow.lidgo.columbia.edu/text/mercury.html)

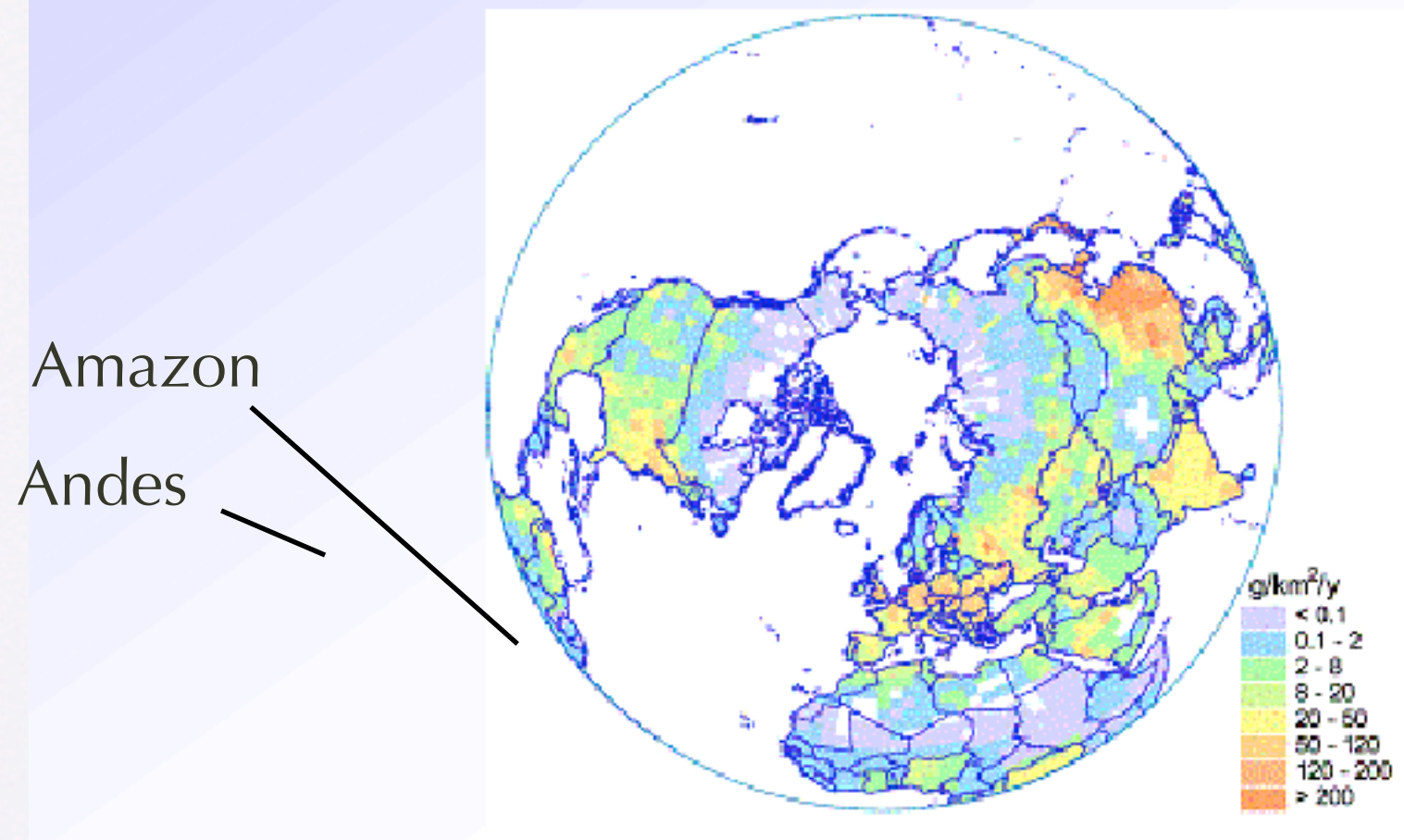
*Why here?*





# Anthropogenic

## Worldwide anthropogenic emission



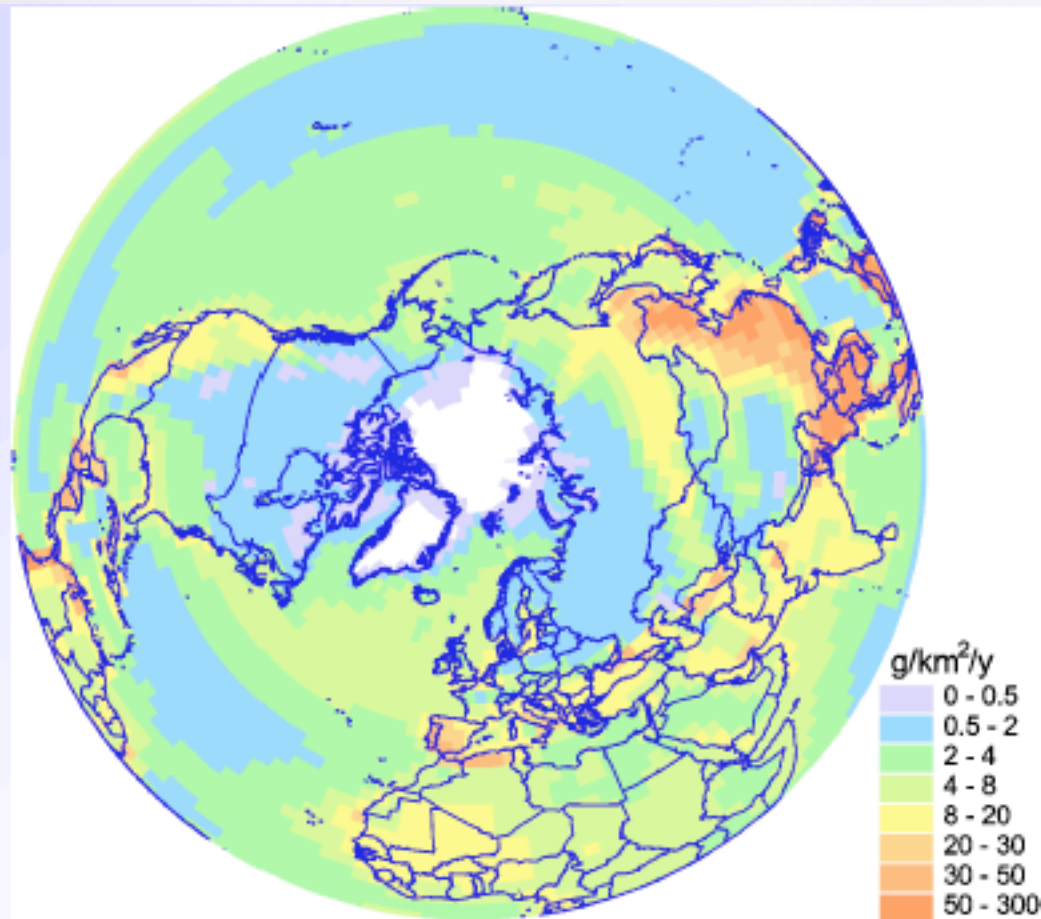
Total worldwide anthropogenic emission for 1995 was 2400 t/yr  
(in the Northern Hemisphere - 1900 t/yr)

(Pacyna and Pacyna, 2002)

- <http://www.delta-institute.org/pollprev/lrtworkshop/LRT%20Presentations/Alexey.Ryaboshapko.pdf>



# Global Natural Emissions



Total worldwide natural emission is **2300 t/yr**  
(in the Northern Hemisphere - **1600 t/yr**)

## Parameterization

Natural emission over the Ocean is proportional to biological primary production of organic carbon.  
Totally – **1500 t/y.**

Natural emission over the continents is a function of mercury content in soils and temperature.  
Totally – **800 t/y.**

**Natural mercury emission is assumed to be in elemental**

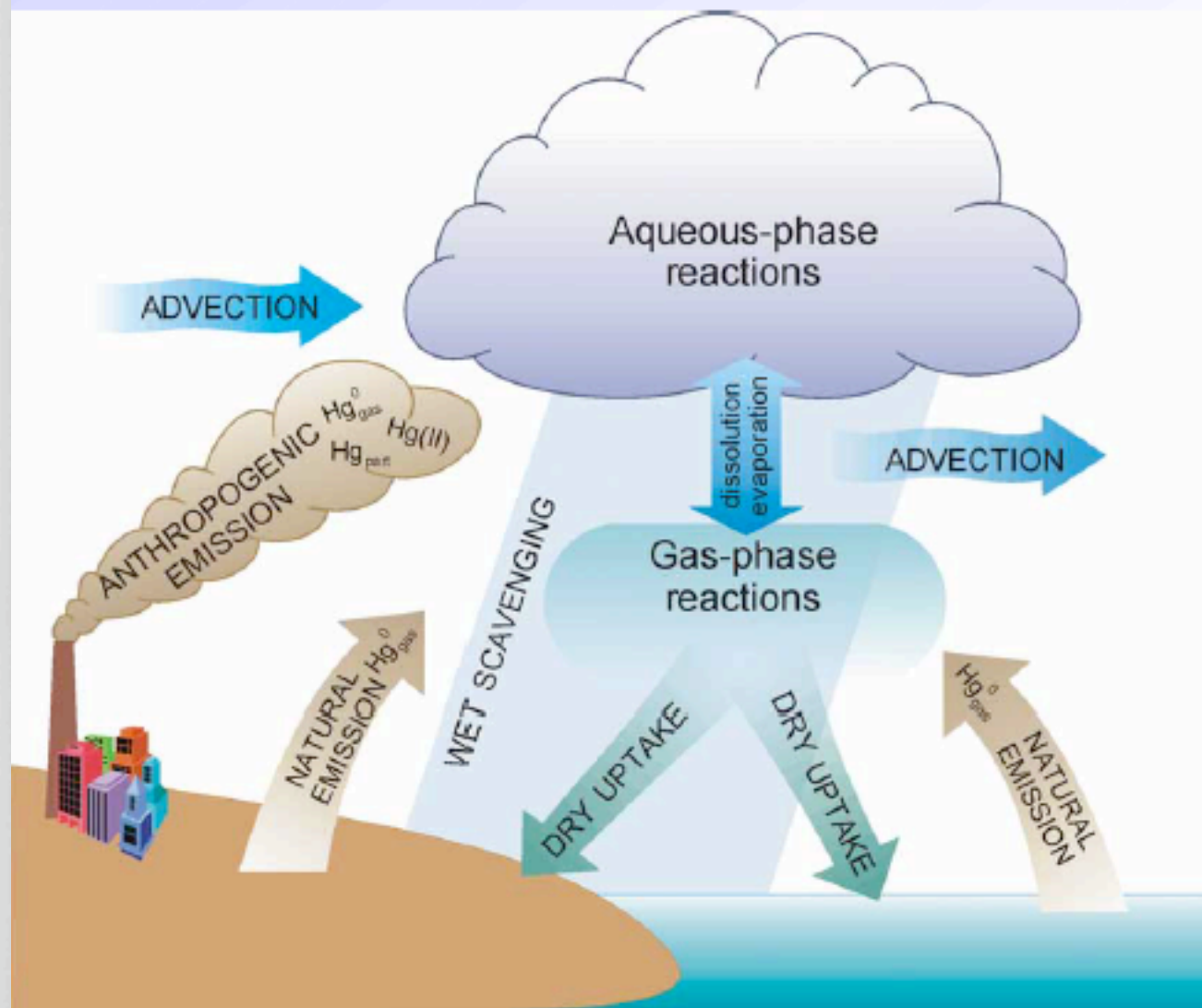
- <http://www.delta-institute.org/pollprev/lrtworkshop/LRT%20Presentations/Alexey.Ryaboshapko.pdf>



# Schematic Processes

*LTR Workshop, Ann Arbor, 2003*

## Mercury atmospheric cycle

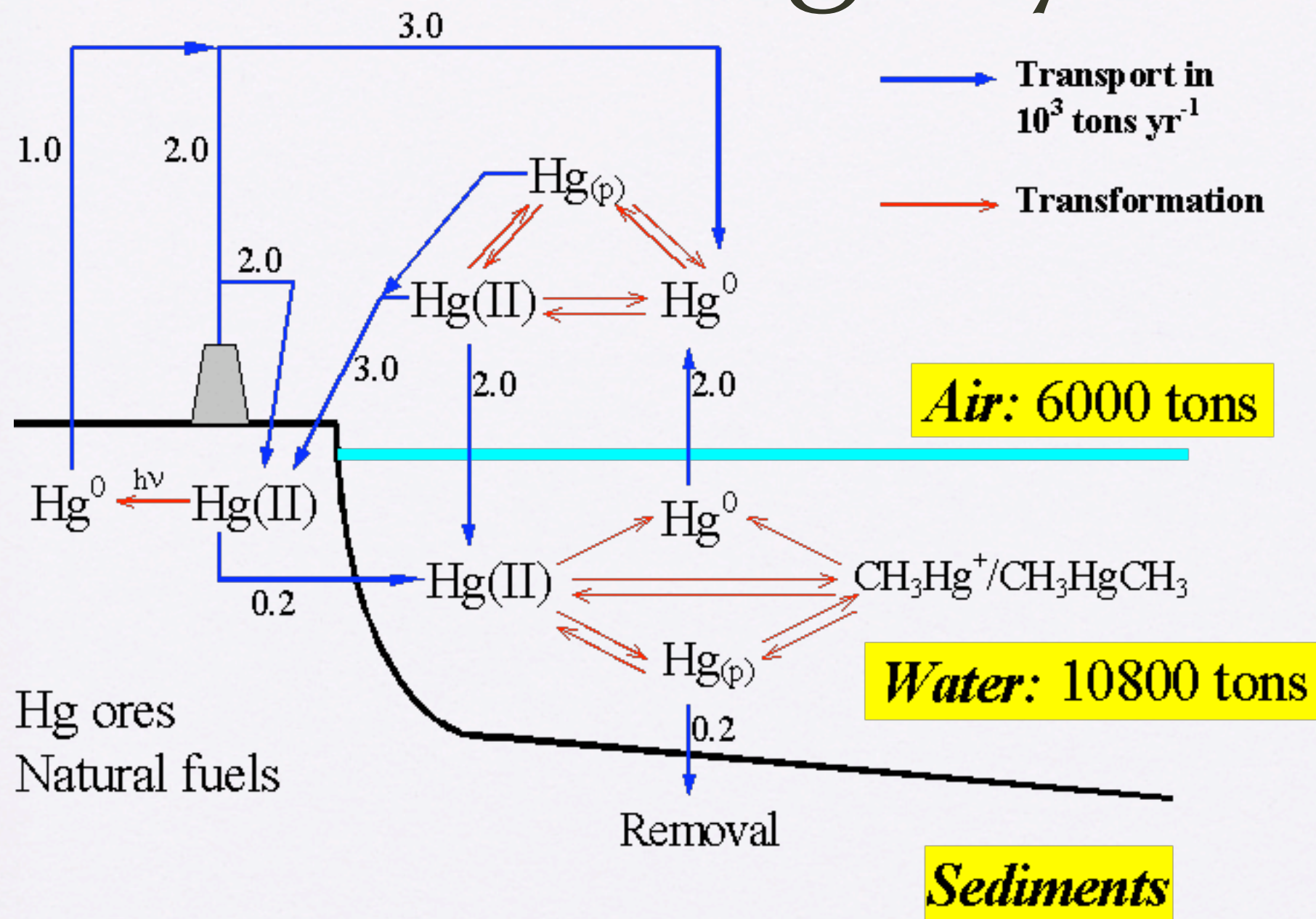


### Basic processes:

- natural and anthropogenic emissions
- dispersion and transport within the atmosphere
- physical-chemical transformations in gaseous and aqueous phases
- wet removal and dry uptake by the underlying surface
- biochemical processes in ecosystems and Hg re-emission to the atmosphere



# Global Hg Cycle





# The Unique Chemistry of Hg

- Hg has highest first ionization potential
- Hg's role as the liquid metal connects to its chemical properties ... don't think "salt" ... think "covalency"  
e.g,  $\text{HgCl}_2$ ,  $\text{HgSO}_3$ , (di-)methyl mercury ... or "amalgam"
- Many chemical pathways may yet be found  
.... existing pathways do not have good rate data



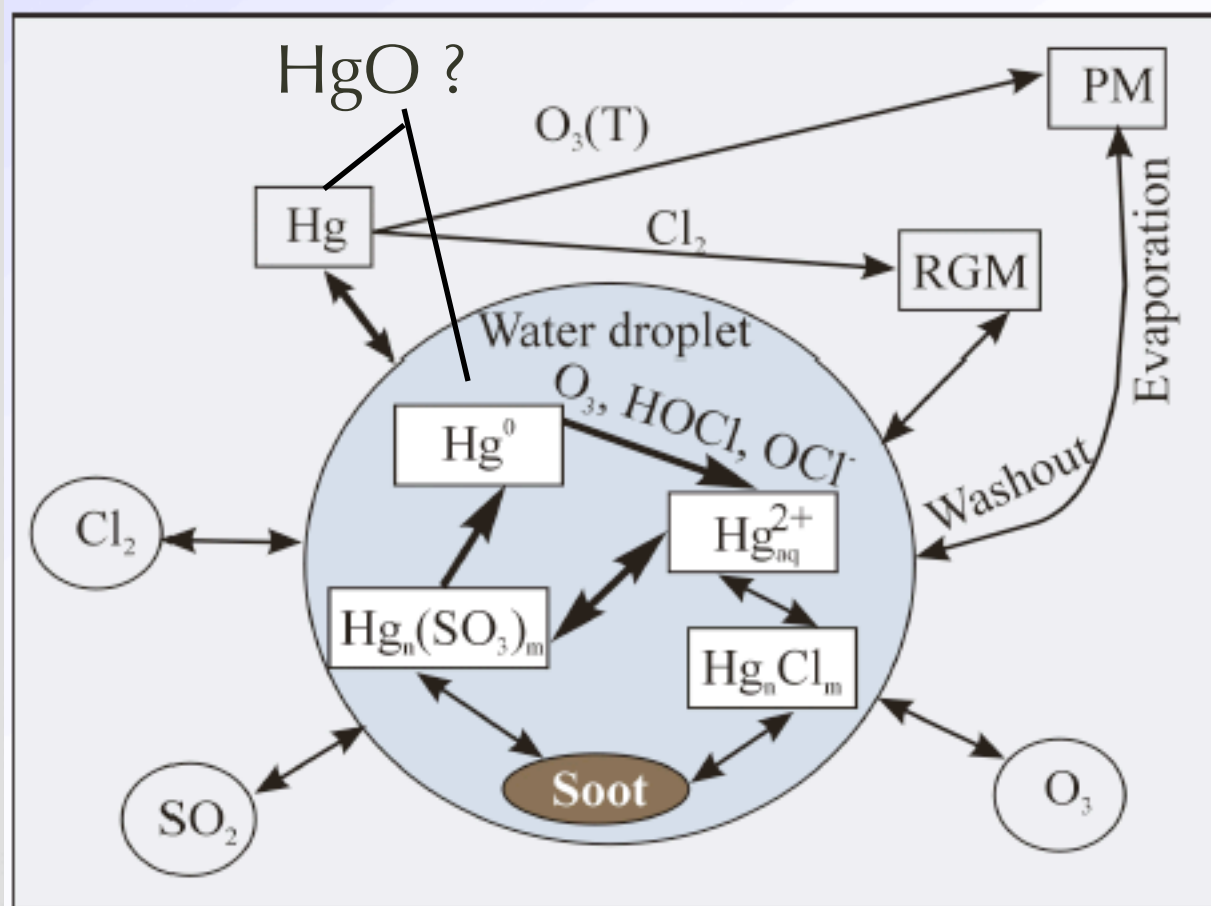
# Hg Chemistry: Alexey Ryaboshapko also Christian Seigneur

*LTR Workshop, Ann Arbor, 2003*

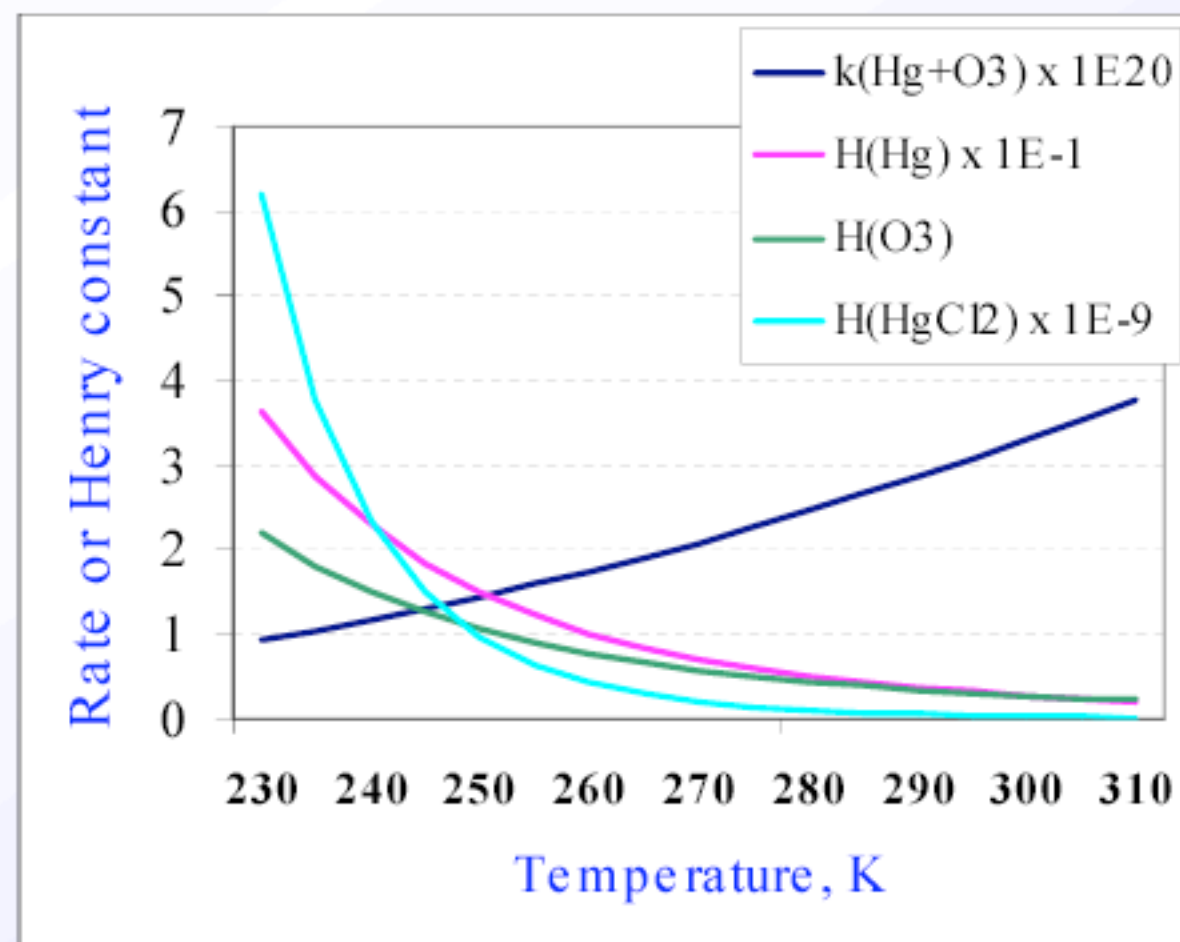
## Chemical transformations of Hg in the atmosphere

### MSCE-Hg chemical scheme

Other bound ? Rates?



### Temperature dependences





# Global Understanding Requires

Christian Seigneur has made pioneering regional and global models of mercury compounds

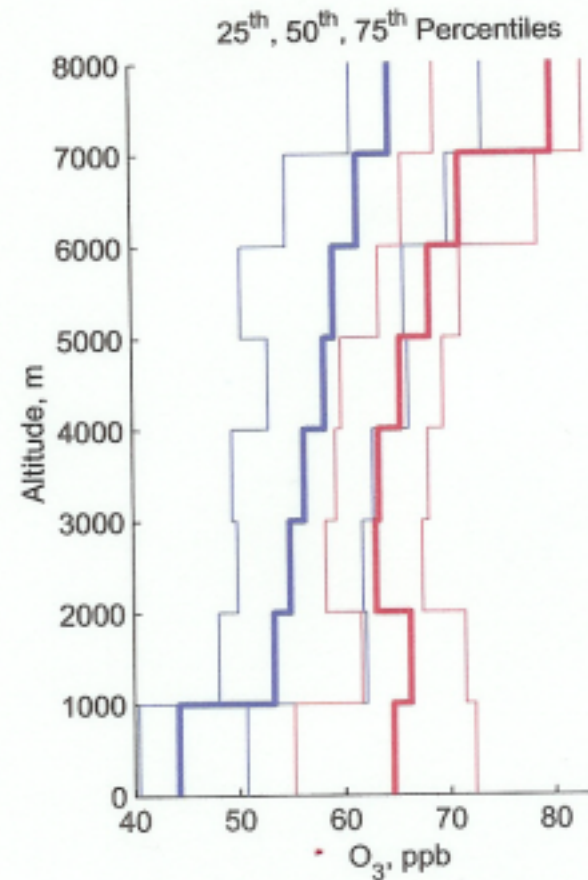
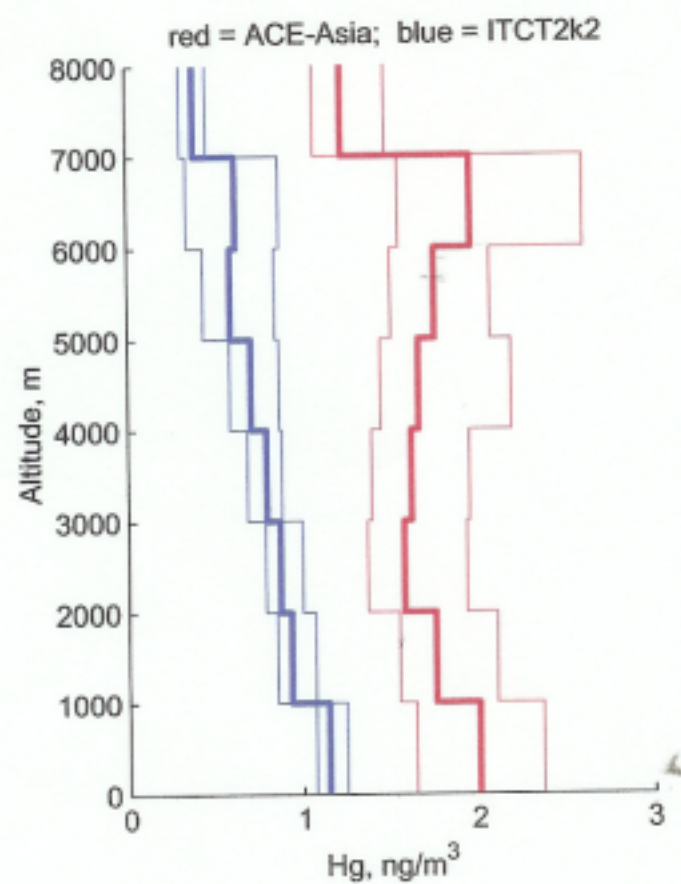
What would be particularly useful would be

- (1) vertical profiles of those species (there is already some evidence that Hg(0) decreases near the tropopause and Hg(II) increases),
- (2) latitudinal gradients (is there more RGM at the lower latitude due to more photochemistry?) and
- (3) seasonal variations.

Christian Seigneur, AER



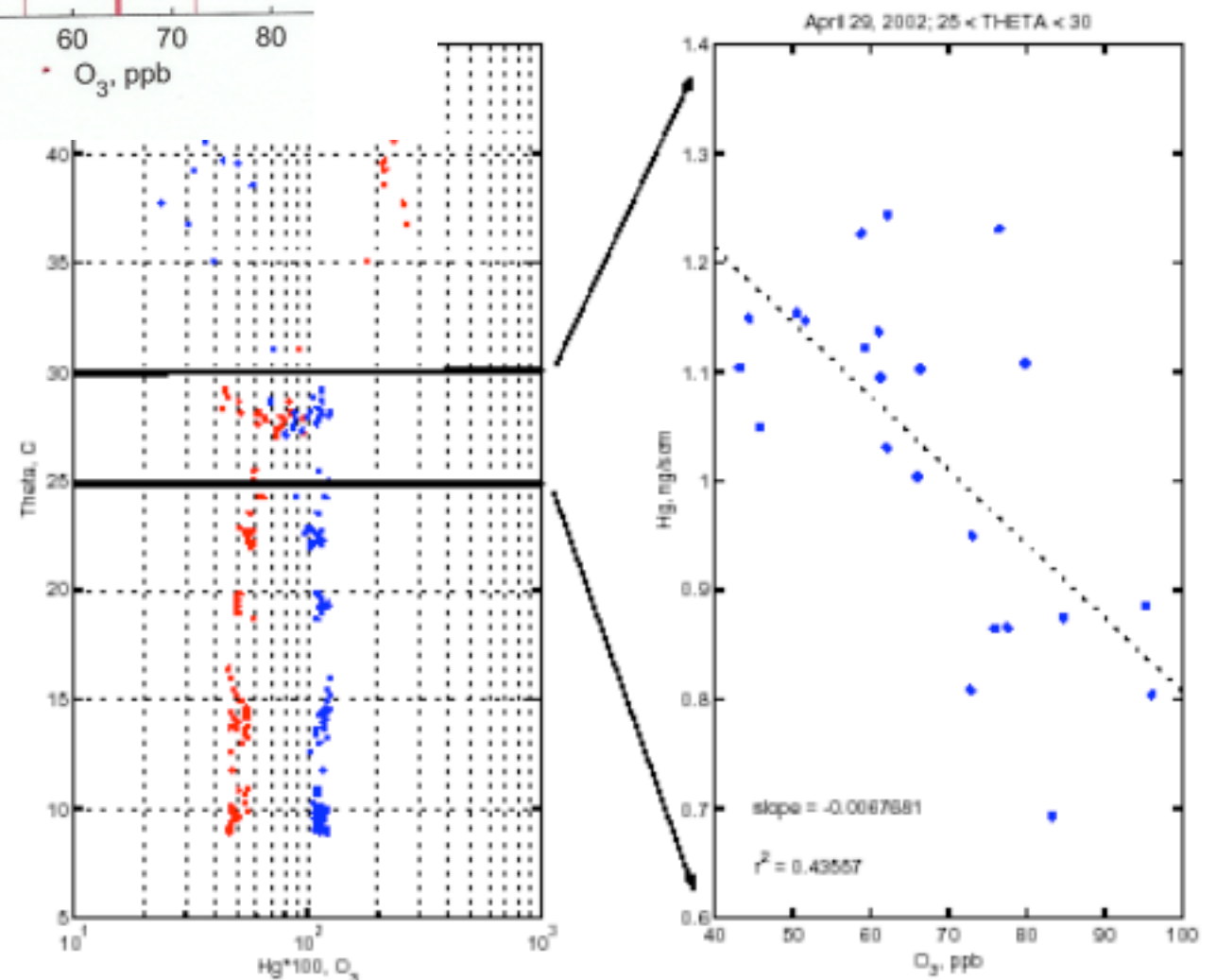
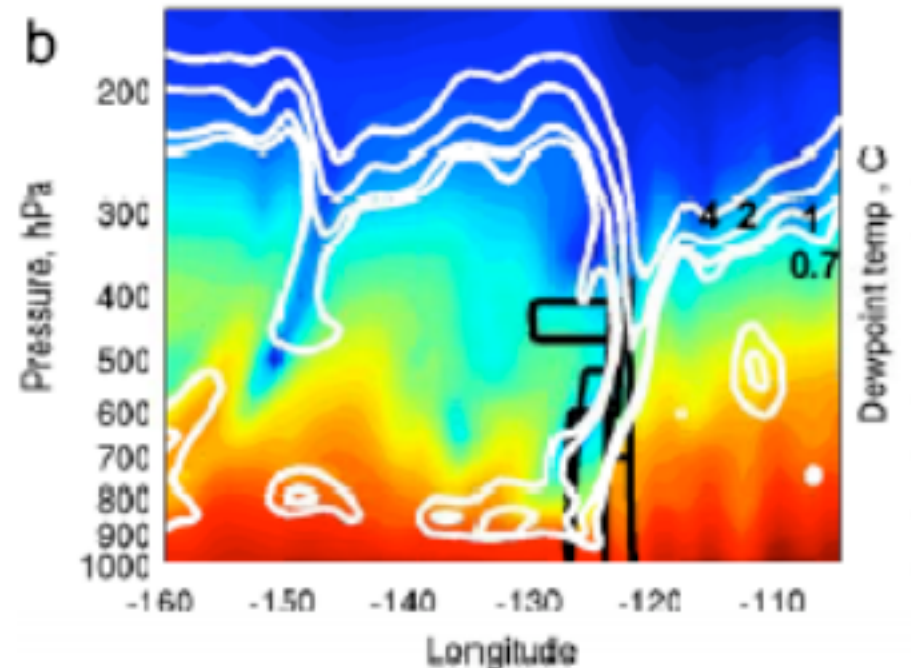
# Average profiles of $\text{Hg}^0$ , $\text{O}_3$



Hg Distribution over Pacific  
at the tropopause

Fieldli, Radke, and Heikes, submitted to JGR

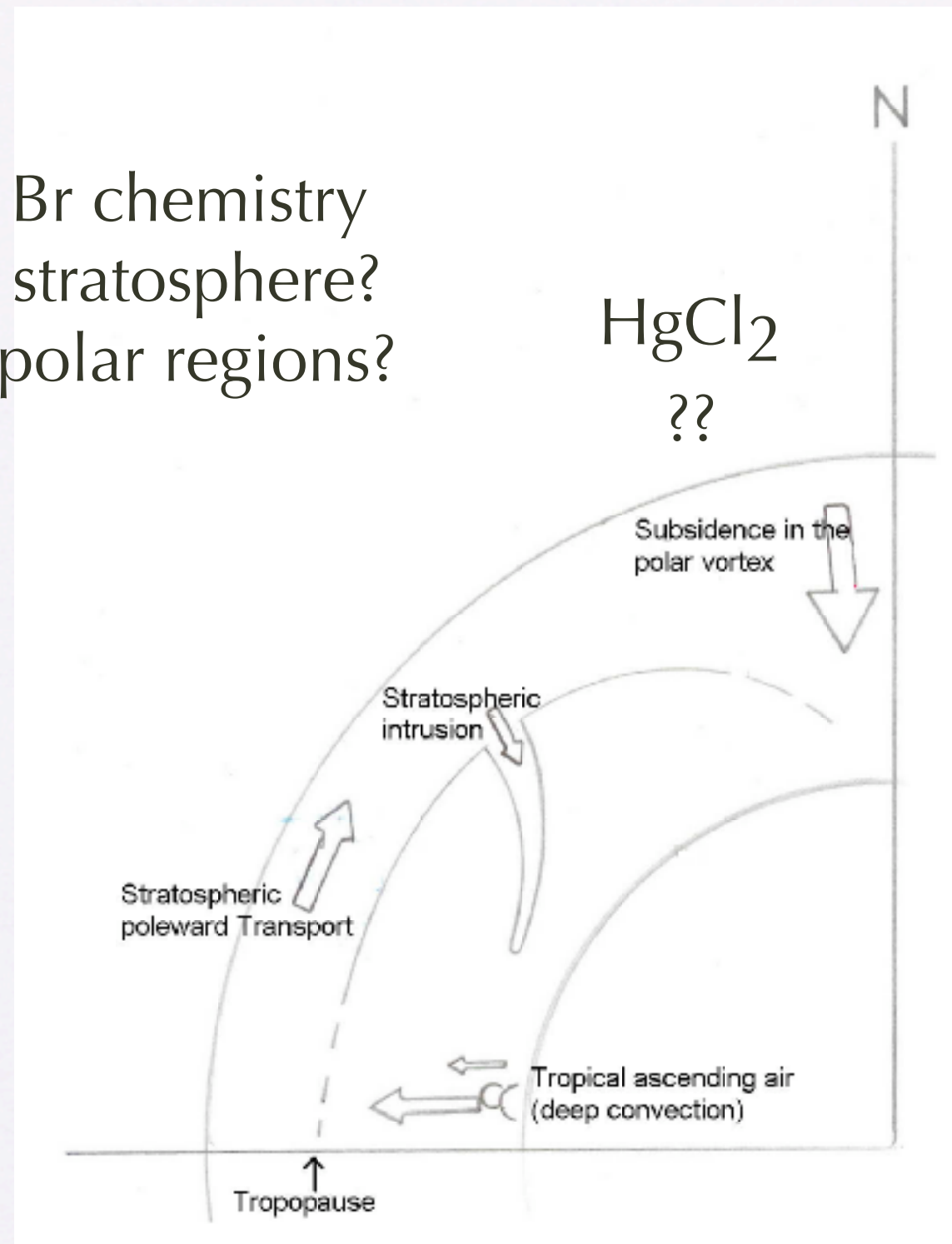
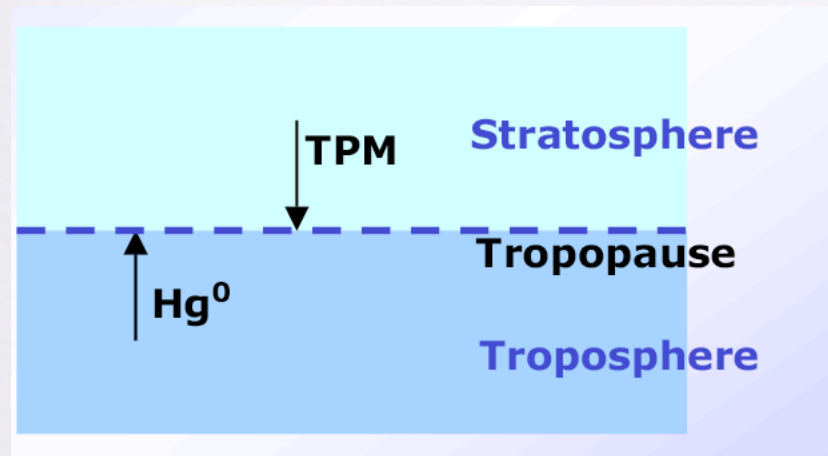
A Tropopause Fold: Detailed  
anticorrelation of  $\text{Hg}^0$ ,  $\text{O}_3$  showing  
stratospheric processing





# Hg Circulation: Hans Friedli, Larry Radke

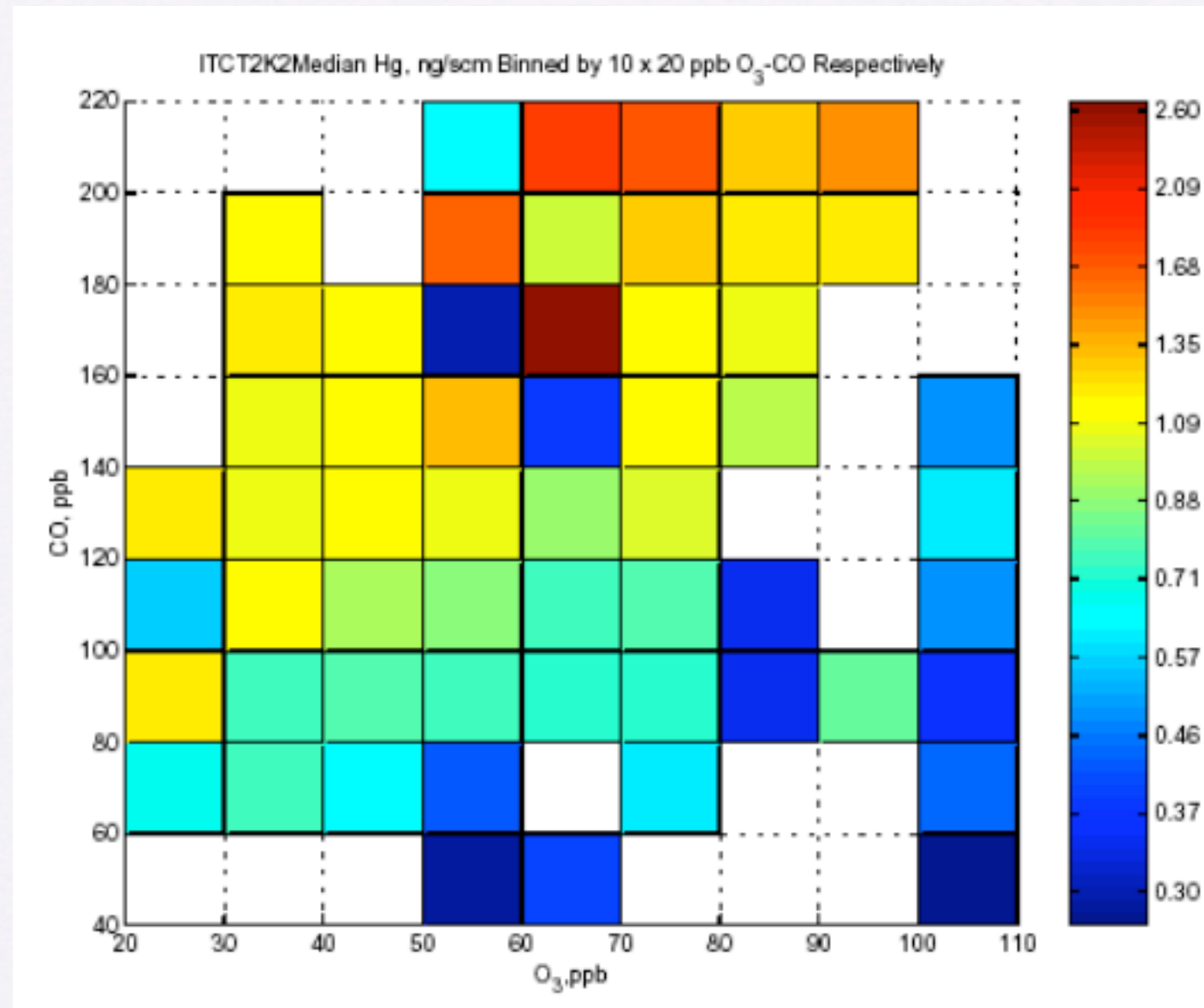
- Cl, Br chemistry
- in stratosphere?
- in polar regions?



Friedli, Radke, and Heikes, 2004



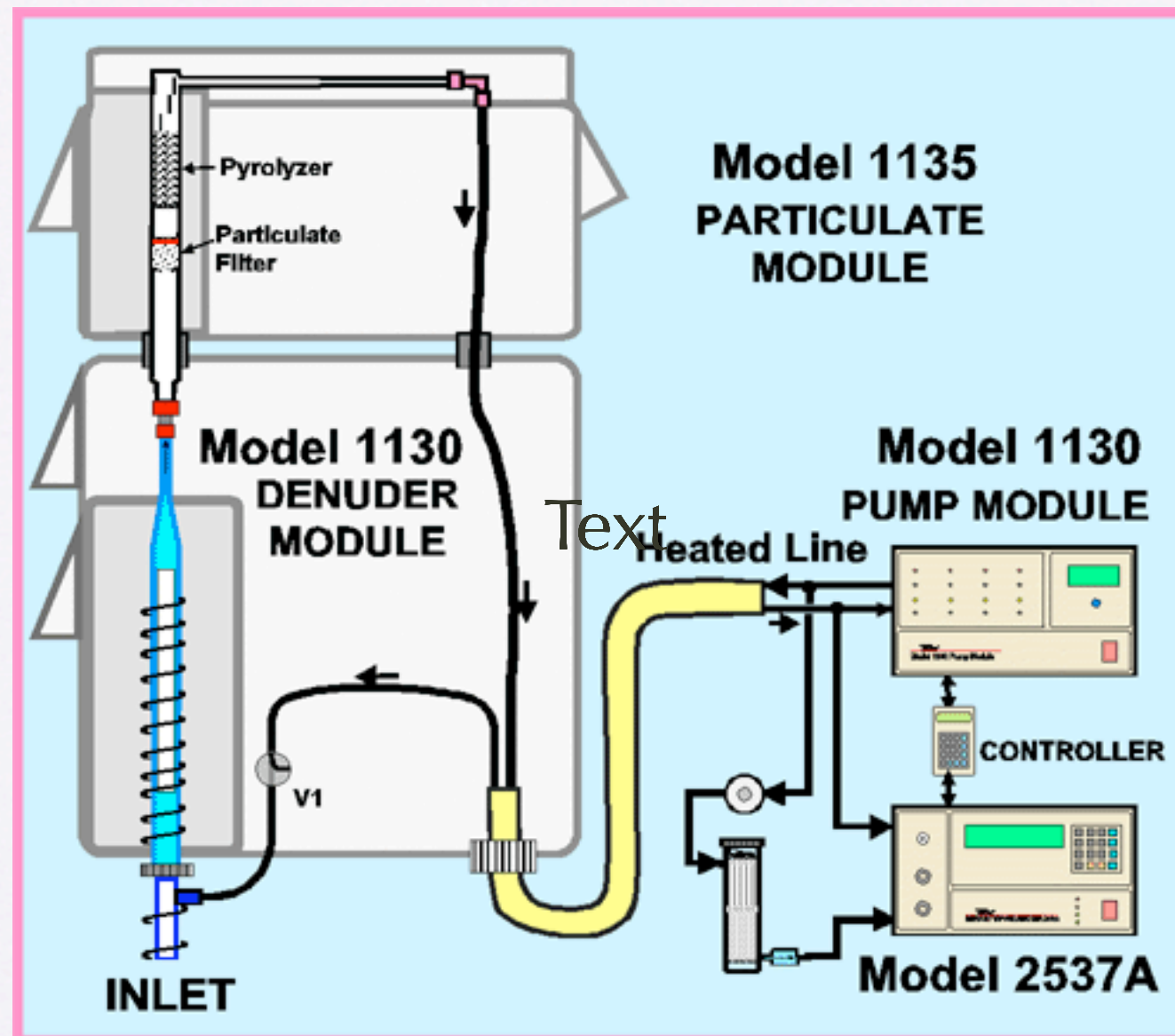
$\text{Hg}^0$  vs  $\text{O}_3$ ...need more  
information... CO helps!



*Friedli, Radke, Hekes, submitted to J.G.R., 2004.*



# Current Technology



*Fluorescence detection of  $\text{Hg}^0$*



# Why there should be continuing Hg measurements on SOFIA

- These measurements look forward 20 years ...
- Hg is now a front-page national issue:
  - Turn off the lights, heat, junk the H<sub>2</sub>-Hummer? ... or prevent subtle long-term pernicious degradation and acute health effects
- Hg has a large global component which may involve important processing and transport in the ozone layer ... these are continuing NASA interests
- Connections to NASA's interest in halogen cycles and ozone-layer
- Both current technology and new development are important
  - continuing measurements vital as Hg questions develop
  - new-instrument intensives for inorganic gas and particle analysis speciation